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16. ABSTRACT

The organic carbon-referenced method of representing sorption of pesticides (K_{OC} approach), including the assumptions inherent in the method and the implications of these assumptions, for soils and sediments is described. Indirect methods of estimating K_{OC} values for pesticides and an alternative approach for determining pesticide distribution coefficients on a surface area basis are presented. To assist potential users in mathematical modeling, a scheme for selecting an appropriate estimation procedure is outlined. Finally, various sources of existing data are identified and described and K_{OC} prediction equations are presented.

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ESTIMATING PESTICIDE SORPTION COEFFICIENTS FOR SOILS AND SEDIMENTS

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INTRODUCTION

Mathematical prediction of the distribution of a pesticide in the environment after its application to agricultural fields requires measured or estimated values of the distribution coefficients. These parameters represent relative concentrations of the pesticide in various phases: liquid (solution phase), solid (sorbed phase) and gas (vapor phase). In this chapter we are concerned with the distribution of pesticides between the solution and sorbed phases, that is, the distribution which dominates the mobility of pesticides associated with soils or sediments.

The importance of pesticide sorption from solution on the environmental fate of pesticides is widely recognized. The physical-chemical nature of the sorption process for a variety of chemicals on organic and mineral surfaces has been exhaustively reviewed (for example, Bailey and White 1964, Hamaker and Thompson 1972, Weber 1972, Weed and Weber 1974, Green 1974). Understanding the mechanisms of specific pesticide-sorbent interactions does not, however, help substantially in assessments of pesticide distribution and impact in the environment, unless sorption information is

integrated with other information on fate processes. Complex mathematical models have been developed to accomplish this integration, but with considerable simplification in the description of individual processes (for example, the ARM and HSPF models of EPA or the CREAMS and SWAM models of ARS/USDA). The incorporation of a large number of processes (physical, chemical and biological) into a complex model usually requires sacrificing detail in the description of any given process. The principal reason for simplification is the lack of independently measured input parameters needed in a detailed mathematical description of the process for a variety of relevant environmental conditions. Such is the case for sorption of pesticides. Although some progress has been made in identifying sorption mechanisms, the complexity of sorption from solution on mixed colloids, such as soils and sediments, has precluded rigorous theoretical analysis of reaction energies. Thus most characterizations of pesticide sorption on soils are empirical in nature. Simplified mathematical descriptions of sorption constitute only a minor sacrifice in the content of information on mechanisms of sorption.

The most attractive simplification is that which can utilize existing or easily developed data on pesticides and soils or sediments to provide sorption estimates with the minimum loss of accuracy. Currently, the approach which is most widely accepted is a linear approximation of the sorbed concentration-solution concentration relationship, and

expression of sorbed concentration with reference to organic carbon content rather than to the mass of the whole soil or sediment (see, for example, Hamaker and Thompson 1972, Chiou et al. 1979, Rao and Davidson 1980, Kenaga and Goring 1980, Karickhoff 1981, McCall et al. 1981, Briggs 1981a and b, Lyman 1982b, and Chiou et al. 1983). An alternative approach is to express sorption on the soil or sediment surface area basis rather than on the mass basis (Pionke and DeAngelis 1980); however, this surface area calculation also weights sorption heavily toward organic carbon content. The organic carbon basis has gained the most acceptance because organic carbon content is commonly measured in soils and sediments, in contrast to surface area which must be estimated from other soil properties. The coefficients obtained by both of these procedures are acceptable as input in the SWAM model (Pionke et al. 1985). However, it is important that the limitations of both simplified sorption approaches be understood by the model user, and inherent errors associated with their use be recognized and even quantified when possible.

The principal objective of this chapter is to present a rational approach for estimation of pesticide sorption coefficients for soils and sediments when such coefficients are not available by direct measurement. The general approach is based on the findings of numerous researchers whose data and conclusions provide some consensus for the recommendations of this chapter. A number of summaries of sorption data and

octanol-water partition data for pesticides have been published in the past several years, increasing the likelihood that at least one of the estimation approaches suggested herein will provide the coefficient required for a given pesticide.

This chapter first describes the K_{oc} approach for estimating pesticide sorption coefficients, including the assumptions inherent in the method and the implications of these assumptions. Indirect methods of estimating K_{oc} values for pesticides are then described and evaluated. Following this, the alternative approach of estimating pesticide distribution coefficients on a surface area basis is presented. Then a scheme to assist a potential user of the model in selecting an appropriate estimation procedure is outlined. Finally, various sources of existing data are identified and described, and K_{oc} prediction equations obtained from various sources are presented.

SORPTION ESTIMATES BASED ON PARTITIONING OF PESTICIDE ON ORGANIC CARBON

A number of simplifying assumptions are inherent in the organic carbon-referenced method of representing sorption of pesticides (K_{oc} approach). The errors in prediction of pesticide distribution which are caused by violation of the assumptions in actual field situations are difficult to assess. The impact and importance of such errors will depend on the objective of the modeling effort and the sensitivity of model

output to variation in sorption parameters. The following discussion will, hopefully, aid the prospective modeler in understanding the advantages and limitations of the K_{oc} approach.

The principal assumptions are (1) equilibrium in the sorption-desorption process, (2) linearity of the sorption isotherm, (3) singularity of the isotherm for sorption and desorption (sorption is reversible), and (4) sorption is limited to the organic component of the soil or sediment. Using the notation of Pionke et al. (1985), the assumed relationship between sorbed concentration C_s (mg pesticide per kg dry soil or sediment) and the solution concentration C_{sol} (mg pesticide per L solution) is

$$C_s = K_d C_{sol} \tag{1}$$

where K_d is the pesticide sorption distribution coefficient having units of L/kg. Whereas C_s represents pesticide sorption per unit mass of dry soil or sediment, C_s can also be adjusted to represent the amount of pesticide sorbed per unit mass of organic carbon, i.e.

$$^{oc}C_s = K_{oc} C_{sol} \tag{2}$$

with K_{oc} also having units of L/kg when the mass of organic carbon is expressed in kilograms. If f_{oc} = (mass organic carbon)/(mass dry soil or sediment), K_{oc} is given by $K_{oc} = K_d/f_{oc}$, and $^{oc}C_s = C_s/f_{oc}$. Thus equation 2 represents a linear sorption isotherm which is referenced to organic carbon content, and K_{oc} is essentially a partition coefficient which

describes the partition of a pesticide between the aqueous phase and the soil organic phase. This approach is appropriate for hydrophobic, non-ionic pesticides with a water solubility less than about 10^{-3} molar. Each of the assumptions inherent in using equation 2 to describe sorption in environmental assessments is discussed briefly.

Assumption of Equilibrium

Although there are a variety of laboratory methods available to measure sorption from solution (Green et al. 1980), the most commonly used method is "batch equilibration" in which a known mass of soil or sediment is equilibrated with an aqueous pesticide solution of known initial concentration until apparent equilibrium in the sorption process is achieved; the pesticide concentration in the aqueous phase is subsequently measured and sorption is calculated from the change in pesticide concentration in solution. It is doubtful that true equilibrium is reached in a few hours for sorbents high in organic carbon, especially if sorption is relatively high. Karickhoff (1981) suggests that the sorption process has a rapid component and a slower component, the rate of the latter depending largely on movement of solute to less-accessible sorption sites; his analysis on one sediment indicated that the rate coefficient for the slow component varied inversely as the sorption partition coefficient.

For most practical applications laboratory measurements

probably produce sorption coefficients which represent macroscale equilibrium quite well, even though equilibrium may not be reached at internal sorbent surfaces. The question to be answered, then, is whether or not an "equilibrium" sorption coefficient measured in the laboratory is appropriate for use in pesticide transport models to represent partition of the pesticide between the aqueous and sorbed states. This question is difficult to answer in a general sense because field systems being simulated may or may not be near equilibrium. In near-static soil-water systems, such as a soil profile at field capacity without evapotranspiration, equilibrium is likely approached, and an equilibrium sorption coefficient may provide a good estimate of pesticide distribution in the soil. Laboratory results of Green and Obien (1969) for equilibration of atrazine in pots of soil at various water contents encourage such a conclusion. On the other hand, during infiltration and redistribution of water in soils, the equilibrium sorption coefficient appears to over-predict pesticide retardation in both laboratory columns and the field. Bilkert and Rao (1983) found that the equilibrium K_d of equation 1 had to be multiplied by a factor of about 0.4 to successfully predict the position of a pesticide peak in soil columns or in a field soil profile. Assuming equilibrium conditions for dynamic systems will result in calculating too much pesticide in the sorbed state for the sorption process and too little in the sorbed state for the desorption process. Pionke et al. (1985) present

a rationale for treating the chemical system in the SWAM Model as an equilibrium system.

Assumption of Linearity

The linear relationship (equations 1 and 2) is a desirable simplification for models as it allows simpler mathematical solutions. For many environmental contexts, e.g. runoff and stream flow, the linear approximation is probably quite accurate and acceptable in terms of other errors associated with the estimation of water and sediment transport. Karickhoff (1984) cites evidence that for hydrophobic compounds sorbed on natural sediments the sorption isotherms are linear if the equilibrium concentration of solute in the aqueous phase is below 10^{-5} molar (1 to 3 ppm) or less than one half the solute solubility in water, whichever is lower. At the higher concentrations encountered in surface soils soon after application of a pesticide to the soil, the linear assumption may result in sorption estimates that are too high by 2- to 3-fold or even more, depending on the extent of isotherm non-linearity and the concentration of solute in solution. In an analysis of data from the literature for a large spectrum of organic compounds and numerous sorbents, Rao and Davidson (1980) found the exponent N, in the Freundlich equation $S = K_f C^N$, to have a mean value of 0.87 with a coefficient of variation of 14.8%. These data included measurements made with solution concentrations far above the 10^{-5} M limit mentioned

previously, but the results emphasize the difficulty of using a single sorption coefficient for all model applications. When N departs significantly from unity (N=1) the apparent K_d may change substantially with changes in pesticide concentration in solution. The error which results from assuming a linear relationship when the Freundlich equation (a power function) is the appropriate mathematical form was given in tabular form by Hamaker and Thompson (1972) and in graphical form by Rao and Davidson (1980).

Assumption of Singularity

An additional uncertainty in the measurement and application of sorption data is the question of whether a single sorption isotherm can represent both sorption and desorption of the pesticide. Numerous investigators have shown, by simply reversing the sorption experimental procedure, that less organic solute is desorbed from the colloid over a given solution concentration interval, than was sorbed initially. This apparent non-singularity, often called sorption hysteresis, has been assessed experimentally and from the literature by Rao and Davidson (1980); they conclude "that while non-singularity of pesticide adsorption-desorption isotherms may often be an artifact, it could be real and significant for certain compounds". Calculation of the error introduced by assuming singularity of a non-singular Freundlich isotherm showed that the error is greater at low solution

concentrations (i.e. far away from the maximum solution concentration at which desorption was initiated) and decreases with increasing non-linearity of the isotherm (Rao and Davidson 1980). Again, perhaps this error is acceptable for a comprehensive environmental model, but the impact should be evaluated by sensitivity analysis.

Assumption of Partitioning on Organic Carbon

The three assumptions above are inherent in the use of equation 1. Adoption of equation 2 as a further simplification is attended by some additional assumptions, which if invalid will introduce more error. It appears that the errors associated with the assumption of partitioning of pesticides on organic carbon may be much larger than those resulting from the first three assumptions. If the model user is to avoid unacceptably large errors which may lead to inappropriate conclusions from model calculations, an awareness of the limits of applicability of the partitioning assumption is necessary.

If equation 2 were to be strictly correct and universal in its application, even if only among so-called hydrophobic organic pollutants, the following assumptions would have to be valid: (1) sorption occurs only on the organic component of the soil, i.e. the mineral component has little or no effect; (2) the organic matter in all soils and sediments is the same with respect to its performance as a sorbent for a given hydrophobic organic solute; (3) the effects of variations in

other factors, such as ionic strength of the solution, pH and temperature, have little or no impact on the amount of pesticide sorbed.

Clearly, none of these assumptions is valid in the strict sense, so that use of organic carbon-referenced sorption will introduce errors, the magnitude of which depends on how severely the assumptions are violated in a given system. Opinions concerning the K_{OC} approach for environmental assessments range from enthusiastic support (Chiou et al. 1979) to skepticism (Mingelgrin and Gerstl 1983). The application of this concept has been proposed and also questioned repeatedly since its introduction relative to pesticides in the early 1960's. Acceptance of the approach has been encouraged by the increasing need for calculation procedures applicable to hundreds of organic chemicals in hazard assessments for a wide range of environmental conditions. The importance and urgency of developing a generalized procedure justifies some sacrifice in scientific rigor and accuracy. On the other hand, theoretical justification for the K_{OC} approach has been provided by Karickhoff (1981, 1984), who identifies the organic carbon-hydrophobic chemical interaction as a "first-order" effect in contrast to the "second-order" effects of other factors of lesser importance. In practice, one must know when "second-order" effects are important. For example, Mingelgrin and Gerstl (1983) challenge the use of the partitioning concept (i.e. that hydrophobic organic chemicals are partitioned

between water and the organic component of soils or sediments in a manner analogous to partitioning between two immiscible solvents); they contend that other mechanisms may play a dominant role, e.g. pesticide-clay-water interactions. These authors illustrate their point by showing the variability in K_{om} (sorption coefficient referenced to organic matter rather than organic carbon) for 12 compounds sorbed on soils or sediments having a wide range of organic matter contents. The largest variation in K_{om} was for parathion (factor of 50 between the largest and smallest value) and the smallest was for dieldrin (factor of 3). The variability that one might anticipate in K_{oc} values for a given compound is indicated by the coefficient of variability calculated for 43 chemicals by Rao and Davidson (1980).

The role of clay minerals in sorption of organic chemicals is addressed quantitatively by Karickhoff (1984). His analysis of a few sets of experimental data suggests that "swelling clays" may have important effects on sorption of some hydrophobic organics in sediments having low organic carbon contents, but when the ratio of clay mineral to organic carbon is less than 30, mineral contributions are masked regardless of the clay mineral content. Thus, further scrutiny of the available data and continued research in this area will help to define applications in which the K_{oc} approach is acceptable.

Finding an Appropriate K_{oc} Value

Once one has decided to use the K_{oc} approach for a reasonably hydrophobic pesticide, the next step is to find the appropriate K_{oc} value. Several tabulations of K_{oc} values for a large number of pesticides are now available; these sources are given in a later section, "Sources of Sorption Data...". If a K_{oc} value is not available for a given pesticide, it may be possible to calculate an approximate K_{oc} from the octanol-water partition coefficient (K_{ow}), if one exists for the pesticide of interest. The K_{ow}-based prediction of K_{oc} and other indirect methods of estimating K_{oc} are presented in the next section. Although additional error may be introduced by indirect approaches, these errors may be no greater than the variability in K_{oc} associated with variation of organic carbon content of soils in a watershed. More research is needed to quantify the relative magnitude of errors contributed by various sources of variation mentioned in this section.

INDIRECT METHODS OF ESTIMATING K_{oc}

As described in the previous section, K_d estimation for uncharged organics can typically be reduced to estimation of K_{oc}, which, when combined with organic carbon content, can yield an estimate of the soil/water partition coefficient, K_d.

The approach used in estimating K_{oc} combines thermodynamic theory and empirical correlation to relate sorption parameters to widely measured properties of pesticides and soils. Theory is used to suggest the mathematical form relating the physical

properties, and experimental data are used to empirically establish constants (by calibration) in the mathematical equation. This approach is far preferable to complete reliance on empirical correlation which precludes extrapolation out of the narrow range of substances or system properties upon which it is based.

K_{oc} can be expressed as a ratio of solute activity coefficients in the aqueous phase, γ^w, and organic carbon phase, γ^{oc}, thus: $K_{oc}=\gamma^w/\gamma^{oc}$. Activity coefficients quantify pesticide "affinity" for a given phase. In considering K_{oc} for a series of uncharged pesticides, one would expect variations in K_{oc} to be dominated by variations in aqueous phase "affinity". This derives from the dissimilarity of the organic solute with the aqueous medium, with variations in γ^w from solute to solute comparable to variations in aqueous solubilities. For uncharged solutes, one would expect much less variability in "affinity" for soil organic matter (γ^{oc}). Water "out-competes" organic solutes for polar sites on soil surfaces, substantially reducing hydrophilic-bonding contributions for uncharged chemicals. Futhermore, lipophilic-interactions with soil organic matter are not highly variable from solute to solute, and their differences in K_{oc} are dominated by γ^w (Chiou, 1983, has recently addressed γ^{oc} variability explicitly). The aqueous phase activity coefficient, γ^w, provides the "thermodynamic link" relating K_{oc} to other solute properties, such as water solubility, molecular

surface area, or octanol/water partition coefficient. Table 1 is a tabulation of semiempirical equations for estimating K_{oc} from solute physical properties. These equations are generally applicable for uncharged pesticides of limited water solubility ($< 10^{-3}$ M) that are not "susceptible" to speciation changes or other complex formation in soil suspensions of interest. Soil organic matter dominance of sorption is presumed, so the ratio of clay mineral/organic carbon must be < 40, otherwise, mineral contributions should be addressed.

SORPTION ESTIMATES BASED ON SPECIFIC SURFACE OF SOIL/SEDIMENT

An alternative to the organic-carbon-referenced sorption approach may be desirable for some pesticide-soil combinations. For example, if the chemical is non-hydrophobic the relationship between K_d and f_{oc} may not be reliable. The K_{oc} approach may also be inappropriate for soils or sediments having a clay:organic carbon ratio which is sufficiently high (perhaps > 40?) for the clay mineral contribution to pesticide sorption to be a significant part of the total sorption.

Pionke and DeAngelis (1980) developed an estimation methodology which allows one to predict K_d values for a large number of pesticides on the basis of the relationship of K_d to either the organic carbon content or the specific surface of the soil or sediment. The specific surface (SS) was calculated from the equation

SS = 100 (% OC) + 2.0 (% clay) + 0.4 (% silt) + 0.005 (% sand).

The coefficients for mineral fractions in the equation were taken from the work of Young and Onstad (1976), while the coefficient for % OC was determined from data presented by Bailey and White (1964), with the assumption that most clay in intact soils would exhibit the surface area of kaolinite (20 m^2/g). The Pionke-DeAngelis method is based on linear regressions between measured K_d values for 35 pesticides and either % OC or SS; the SS calculation is heavily weighted toward organic carbon, i.e. % OC dominates except where % clay is large and % OC is very small. It was designed to give results similar to the K_{oc} calculation (Pionke, personal communication). For a diverse group of pesticides the equation $K_d = mSS$ gave consistently higher coefficients of determination than did the equation $K_d = m$ (% OC) + b, thus the authors recommended the surface area approach. To extend the relationship between K_d and soil surface area to other pesticides which were not included in the original data set, Pionke and DeAngelis developed curves relating m values from the two equations to published R_f values from soil thin-layer chromatography (Helling 1971). Since R_f values were available for about 100 pesticides, the R_f-m relationship obtained for the original group of pesticides could then be used to predict m values for many other pesticides for which R_f values had been measured. The procedure requires an assumption that the standard soil on which the R_f values were measured (Hagerstown silty clay loam) is reasonably representative of the soils for

which the predictions of pesticide sorption are to be made. The authors present data of Helling (1971) which show that R_f values for the Hagerstown soil were representative of the average mobility of 13 pesticides on a number of fine textured soils. However, the Hagerstown data did not adequately represent R_f results for two coarse-textured soils. While the soil thin-layer procedure is a good way to characterize relative mobilities of a large number of pesticides, it is risky to assume that the relationship between R_f and m values can be applied to any soil of interest, even if the soil is fine textured. In the present context we are interested in predicting an adsorption coefficient for a specific pesticide on a specific soil, which may not be well-represented by the average mobility of the pesticide on many soils. However, in spite of this principal limitation of the Pionke-DeAngelis method, the approach does provide an alternative for pesticide-soil combinations for which the K_{OC} method appears inappropriate. The reader is encouraged to consult the paper by Pionke and DeAngelis for details.

SELECTING A SORPTION COEFFICIENT FOR A GIVEN COMBINATION OF PESTICIDE AND SOIL OR SEDIMENT

In the event that it is not possible or practical to measure an appropriate distribution coefficient for a specific pesticide-soil combination, then an estimation procedure must be followed. The following decision sequence provides a

systematic approach to obtaining an estimate of a sorption coefficient.

Required information:

1. The nature of the chemical. Five useful groupings of chemcials are: (a) hydrophobic (solubility in water less than 10^{-3}M or about 300 mg/L); (b) sufficiently polar so that solubility in water exceeds 10^{-3}M, but not cationic or a weak acid or weak base; (c) a weak base; (d) a weak acid; (e) a cation.
2. Soil or sediment properties. The nature of the pesticide and the associated procedure used to obtain an appropriate sorption coefficient will determine what soil or sediment properties are required. In general, the order of priority for required data will be:
   (a) organic carbon content
   (b) clay, silt and sand contents
   (c) pH

Organic carbon content is required for both the K_{oc} approach and the surface area approach. Percentages of the various textural separates are required for the surface area approach and will aid in estimating the mineral contribution to sorption. The pH is needed only if the pesticide of interest is an acid or base.

A scheme for obtaining a sorption coefficient for a given

pesticide in a given soil or sediment is shown in Figure 1. Each decision or action step is numbered for easy reference in the following discussion. While an attempt has been made to provide a definitive procedure that can be followed by anyone with a basic understanding of the chemistry of pesticides and soils, there are a number of points of uncertainty that will be encountered in using the scheme. For example, the definition of "hydrophobic" is somewhat arbitrary, but the criterion of $<10^{-3}$M solubility in water is a useful, though perhaps conservative, upper boundary for hydrophobic compounds. Other criteria for decisions, such as in steps 2 and 11 are based on experimental evidence but may not be appropriate for all soil-pesticide combinations. Experience in using the scheme in Figure 1 should lead to procedural improvements.

Some brief explanations or directions associated with several steps in Figure 1 are given below to assist in the use of the scheme.

Steps 1, 8, 9, 10 and 11: The use of the K_{oc} approach is most appropriate for organic chemicals of limited solubility in water. Karickhoff (1984) has suggested a solubility of $<10^{-3}$M, or about 100 to 300 mg/L for most pesticides. K_{oc} values are available in the literature for many chemicals with much higher solubilities in water, but the reliability of the K_{oc} approach is more questionable for these pesticides than for hydrophobic chemicals.

There are unique problems associated with the estimation

of sorption coefficients for weak acids and weak bases due to significant changes in sorption mechanism and quantity sorbed with changes in soil pH. Some generally-accepted assumptions for such pesticide-soil systems provide guidelines for estimating K_d values for weak acids and weak bases: (a) The pH at colloid surfaces is lower than in a bulk soil-water suspension, such as in the 1:1 soil:water slurry often used for pH measurement. A reasonable estimate of surface pH is one to two pH units lower than the bulk suspension pH. (b) In aqueous solutions the ratio of molecular to ionic species is 1:1 when pH = pK_a. Most weakly acidic pesticides are in predominantly ionic (negatively charged) form at the pH of most agricultural soils, while most weakly basic pesticides are in molecular form. In either case as soil pH decreases toward a value equal to the pK_a of the pesticide, sorption tends to increase because the acidic pesticide has more of the molecular species at low pH and the basic pesticide has more of the protonated (positive) ionic species at low pH. The colloidal surfaces of most agricultural soils have a net negative charge and thus have an affinity for positively charged species of bases but not much affinity for negatively charged species of acids. Pionke and DeAngelis (1980) adopted the following approximations: 50% of the basic pesticide is positively charged when the measured soil suspension pH minus 1.0 equals the pk_a, and 50% of the acidic pesticide is negatively charged when soil suspension pH equals the pK_a. These workers suggest

that if measured pH - 2 is one or more pH units above the pK_a of the pesticide, the effect of pH on K_d can be considered insignificant. This limiting criterion can be summarized by $pK_a \leq$ (soil pH - 3). In the absence of other more rational approaches, the above rule is adopted for weak bases in the scheme in Figure 1 (see step 11). Many acidic pesticides at prevailing soil pH values are negatively charged and thus are not hydrophobic. Use of the K_{oc} approach is inappropriate in this case, hence a measured K_d for a specific application is required. Values of pK_a for several basic pesticides are given by Pionke and DeAngelis (1980).

Steps 2 and 7: The K_{oc} approach assumes no contribution of the mineral fraction of a soil or sediment to sorption of a hydrophobic chemical. However, when the organic carbon content of the sorbent is low relative to the clay content, the clay may contribute to sorption (Minglegrin and Gerstl 1983, Karickhoff 1984). Karickhoff (1984) found a threshold for swelling-clay contribution to sorption at a f_{cm}/f_{oc} ratio of about 30/1 for clay mineral fraction (f_{cm}) to organic carbon fraction (f_{oc}). This ratio can be expected to vary with clay type, swelling clays being more active in sorption than non-swelling clays. At the present time there is no quantitative method of correcting for mineral contribution to sorption, but a threshold of about 40 for f_{cm}/f_{oc} may be a reasonable value to adopt in view of the suggestion by Karickhoff of 25 to 60 for neutral organics with polar functional groups and >60 for nonpolar organics.

Steps 3 and 4: Sources of K_{OC} and K_{OW} data for a large number of pesticides are given in a later section in this chapter. It is anticipated that such data will be developed in the near future for all commercially available pesticides used on field crops.

SOURCES OF SORPTION DATA, OCTANOL-WATER PARTITION DATA AND OTHER INFORMATION PERTINENT TO SORPTION ESTIMATES

It is our intention in this section to direct the reader to the principal published summaries of pesticide sorption data. New data continue to be published so that any published summary is soon dated. It would be a major service to model users if some agency would undertake the on-going accumulation, categorization and development of a computer retrieval system for all environmentally relevant distribution coefficients. An admirable attempt in this direction has been initiated by Dr. Ralph Nash of the Pesticide Degradation Laboratory, ARS-USDA, Beltsville, Maryland.

A well-organized and well-documented data set which could be easily accessed by potential users would have tremendous value in the future. However, at the present time one must rely on existing published summaries of data or find individual published research papers dealing with specific chemicals of interest. Several of the summary-type papers have presented regression equations, calculated with the data base at hand, which further summarize the relationships of measured K_d or K_f

to organic carbon content or the relationship of K_{oc} to K_{ow} or solubility in water. In general, such regression equations summarize a large body of data obtained from various sources; use of such equations has the advantage of generality of application but the disadvantage of incorporating a high level of variability which is inherent in the procedure of lumping data from many sources.

The following selected sources of data are given in the order that the manuscripts were first made available or published. Original measured sorption data are included in a number of summaries of sorption data. Usually the source of the original data is cited in the summary paper.

1. Hamaker and Thompson (1972). This comprehensive paper on sorption processes in soils provides the following tabular data for a large number of pesticides:
   - Average K_d and C.V. (coefficient of variation)
   - Average K_f and 1/n (Freundlich constants) and C.V.
   - Average K_{oc} derived from K_d or K_f and the C.V. for K_{oc}
   - Range of organic carbon contents (%) of soils or sediments in sorption experiments
   - Range of pesticide concentrations in solution
   - Equilibration times
   - Temperatures
   - Number of soils used in each study

The authors have provided separate data summaries for soils containing more than 8.7% organic carbon.

2. Kenaga and Goring (1980) — first made available in a symposium proceedings in 1978. This listing of 170 chemicals (principally pesticides) provides average values of K_{OC}, K_{OW}, water solubility (WS) and bioconcentration factor (BCF). No estimate of variability is given but references to the original sources of the data are provided. Using the appropriate data for all chemicals in the table, Kenaga and Goring calculated regression coefficients for the linear equations relating pairs of coefficients (in log form). For example:

$$\log K_{OC} = 1.377 + 0.544 \ (\log K_{OW}) \qquad (3)$$

$$\log K_{OC} = 3.64 - 0.55 \ (\log WS) \qquad (4)$$

The correlation coefficients for equations 3 and 4 were 0.86 and -0.84 respectively, and the 95% confidence limits on log K_{OC} were ± 1.37 and ± 1.23 respectively. The considerable prediction error represented by these confidence intervals is likely the result of including such a wide variety of chemicals in a single regression. The prediction error is expected to be much less for regressions accomplished with chemicals of similar structure and properties.

3. Rao and Davidson (1980). This summary provides mean values of K_d or K_f and the associated derived values

of K_{oc} and ln K_{oc} (they used the base e logarithm here) for 44 chemicals, most of which are herbicides. Coefficients of variation and the number of soils included in the measurements for each chemical are also given. In addition, K_{ow} values are provided for 67 chemicals. A linear regression of log K_{oc} on log K_{ow} for the sorption data of 13 pesticides presented in this paper resulted in the equation

$$\log K_{oc} = 1.029 \log K_{ow} - 0.18 \qquad (5)$$

with $r^2 = 0.91$. This equation differs considerably from equation 3 (above) of Kenaga and Goring.

It is of interest that the coefficient of variation for ln K_{oc} was found to be much lower than the C.V. for K_{oc} for most pesticides. Also the geometric mean of K_{oc} was generally lower than the arithmetic mean. The detailed data from which mean values were derived by Rao and Davidson (1980) are given in an appendix of a report by Rao et al. (1983).

4. Pionke and DeAngelis (1980). This paper is summarized in a previous section entitled SORPTION ESTIMATES BASED ON SPECIFIC SURFACE OF SOIL/SEDIMENT. Tabular sorption data are presented for 35 pesticides. Distribution coefficients for these chemicals can be calculated for a given soil from the organic carbon content (% OC) or the specific surface area (SS, m^2/g) using the regression equations

K_d = m (% OC) + b or K_d = m (SS). Also, the relationships developed for the 35 chemicals can be used to determine K_d values for about 100 pesticides for which soil-thin-layer chromatography R_f values are available.

5. Briggs (1981a). This paper seeks to establish a general relationship between the partition coefficients for organic chemicals sorbed on soil organic matter (K_{om}) and the octanol-water partition coefficients (K_{ow}) of the same chemicals. The K_{om} of Briggs is related to K_{oc} by $K_{om} = K_{oc}/1.724$. Initially, sorption measurements for 72 chemicals were accomplished on four soils at four solution concentrations. The resulting sorption isotherms were sufficiently linear to justify calculation of K_{om} values for each chemical on each of the four soils (organic matter percentages ranged from 1.09 to 4.25%). This group of chemicals included only 12 pesticides, most of which were substituted urea compounds. Subsequent measurements of K_{om} for other chemicals (including some pesticides) on one or more soils were made at only one solution concentration. Tabular values of log K_{om}, log K_{ow} and log WS are given for all chemicals. Also, the linear regression of log K_{om} on log K_{ow} was accomplished for each chemical group (13 groups). The average correlation

coefficient for all of the regressions was 0.95.

Other recent papers present original measured K_{om} or K_{oc} results for a limited number of pesticide-soil combinations. For example, Briggs (1981b) examined the relationship of K_{om} and K_{ow} for 24 chemicals, 12 of which were pesticides; this study involved 17 soils, having organic matter contents varying from 0.19% to 6.62% (corresponding to organic carbon contents of 0.11% to 3.84%). The chemicals were mostly substituted phenyl-urea herbicides. Another recent study (Rao et al. 1983) included five herbicides and three insecticides sorbed on seven soils and particle-size separates of the same soils. K_{oc} values calculated from measured sorption on these soils were compared with K_{oc} values from the literature and with values calculated from pesticide solubility and melting point. Two-fold differences in K_{oc} values for a given chemical existed between the three sets of data. Karickhoff (1981) found that variation between measured and computed K_{oc} values was comparable to deviations in measured K_{oc} values reported for a given compound on widely different sediments or soils.

Index Of Pesticide Sorption And Partition Data In Published Summaries

To assist potential model users in finding sorption coefficients (K_{oc} or K_{ss}) or octanol-water partition coefficients (K_{ow}) for specific pesticides, we have provided an

alphabetical listing of the pesticides for which such data are available in the above sources. The list is given in Appendix A. As additional sources of data become available, the list can be updated periodically by the user. Commonly accepted chemical names have been used.

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APPENDIX A: Pesticide K_{oc} and K_{ow} Values from Published Data Summaries[1]

Sources of data are indicated by the letters in brackets after table values; the source references are given at the end of the table. An attempt was made to round off numbers to avoid an inference of unrealistic precision, but the data are presented here with no evaluation of either accuracy or precision. The reader is encouraged to check the original sources for details.

Chemical	K_{oc}	K_{ow}
Alachlor	190[B]	830[B], 434[C]
Aldicarb	42[E]	5.0[C], 37[E]
Aldicarb sulfone	3[E]	0.3[E]
Aldrin	410[B], 48600[E]	25,000,000[E]
Altosid	-	176[C]
Ametryn	380[A], 392[B], 388[C]	-
Amiben	190[C]	-
Asulam	300[B]	-
Atrazine	102[A], 149[B], 163[C], 111[G]	476[B], 212[C], 226[C]
Azobenzene	1340[E]	6610[E]
Benefin	10700[B]	-
Benomyl	-	264[C]
Bentazon	0[B]	220[B]

Bifenox	-	174[C]
Bromacil	72[B], [C]	104[C]
Butralin	8200[B]	-
Captafol	2070[E]	6760[E]
Captan	198[E]	224[B], 33[C], 347[E]
Carbaryl	230[B], 298[G], 104[E], 121[F]	230[B], 651[C], 209[E]
Carbofuran	29[C], 40[G]	40[B], 207[C]
Carbofenthion [D][2]	-	-
Carbon tetrachloride	-	436[B]
Carbophenothion	45400[B]	-
Chloramben	21[B]	13[C]
Chloramben, methyl ester	507[B], [A]	-
Chloramben, NH_4^+ salt	13[A]	-
Chlorbromuron	217[A], 460[B], 996[C], 377[E], 364[F]	1230[E]
Chlordane	-	2110[C]
Chlorfenvinphos	293[E]	1260[E]
Chloroneb	1160[B], 1650[C]	-
Chloropropham	816[C]	1160[C]
6-Chloropicolinic acid	9[B]	0.02[B]
Chloroxuron	3200[B], 4340[C]	-
Chlorpropham	590[A],[B], 245[A],	

	923[A], 816[C]	
Chlorpyrifos	13600[B]	97700[B], 2060[C], 66000[C], 129000[C]
Chlorpyrifos, methyl	3300[B]	14750[B], 1970[C], 20400[C]
Chlorthiamid	107[B], 98[C]	-
Chlortoluron	104[E], 105[F]	257[E]
Ciodrin	75[C]	-
CIPC [D]	-	-
Crotoxyphos	173[A], 170[B]	-
Crufomate	-	2780[B]
Cyanazine	200[B], 116[G]	150[B]
Cycloate	345[A],[B]	-
2,4-D	32[A], 23[A], 20[B],[C]	37[B], 416[C], 443[C], 646[C]
2,4-D, amine	109[C]	-
Dalapon	-	6[B], 5.7[C]
Dalapon, Na salt	-	1[C]
DBCP	129[B]	-
DDD	-	1047000[B], 115000[C]
DDE p,p	-	490000[C]
DDE	-	583000[B], 73400[C]
DDT	131000[A], 355000[A], 229000[A],	960000[B] 370000[C] 1549000[C]

	238000[B],	
	243000[C],	
DDT p,p	-	1549000[C]
DDVP	-	195[C]
Dialifor	-	49300[B], 49000[C]
Diallate	1900[B]	-
Diamidaphos	32[B]	-
Diamidfos	30[A]	-
Diazinon	227[E]	1052[C], 1288[E]
Dicamba	4[A], 0.4[B], 2[C]	3[C]
Dichlobenil	164[A], 235[B],	787[C]
	224[C]	
Dichlofenthion	-	137000[B],
		138000[C]
3,6-Dichloropicolinic		
acid	2[B]	-
Cis-1,3-Dichloro		
propene	26[A], 23[B],	-
	798(Telone) [C]	
trans-1,3-Dichloro		
propene	28[A], 26[B],	-
	1380(Telone) [C]	
Dichlorovos	-	25[B]
Dicifol	-	3460[C]
Dieldrin	12780[E]	4930[C], 1585000[E]
Diflubenzuron	6790[B]	-

Dimethoate	9[E]	0.51[B], 6[E]
Dimethyl amine	435[C]	-
Dinitramine	4000[B]	-
Dinoseb	124[B]	4900[B], 198[C]
Diphenylamine	598[E]	2630[E]
Dipropetryn	1170[B], 1180[C]	-
Disulfoton	1780[B], 1600[C]	-
Diuron	902[A], 400[B], 383[C], 161[E], 191[F],534[G]	94[B], 650[C], 479[E]
DMU	286[E], 319[F]	871[E]
DSMA	770[B]	-
Endrin	-	218000[B], 1620[C]
EPTC	283[A], 240[B]	-
Ethion	15400[B]	-
Ethoxychlor	-	1180[C]
Ethylene dibromide	32[A], 44[B]	-
Fenamiphos	329[E]	1510[E]
Fenitrothion	-	2400[B], 2300[C]
Fenuron	0.6[A], 27[B], 42[C], 13[E], 26[F]	10[B], 9[E]
Fluchloralin	3600[B]	-
Fluometuron	175[B], 66[E]	22[B], 263[E]
Folpet	1850[E]	4270[E]
Fonofos	770[G]	-
Glyphosate	2640[B]	-

HCB	-	1660000[C]
Heptachlor	-	7370[C]
Hydroxy atrazine	888[A]	-
Ipazine	2570[A], 1660[B]	2900[B]
Isocil	130[B]	-
Isopropalin	75250[B]	-
Leptofos	-	4120[C]
Leptophos	9300[B]	2020000[B], 2042000[C]
Lindane	1940[A], 911[B], 1080[C]	643[C]
Linuron	653[A], 820[B], 863[C], 267[E], 229[F]	154[B], 575[E]
Malathion	1800[C]	780[B], 230[C], 776[C]
Methazole	2620[B]	-
Methiocarb	207[E]	832[E]
Methomyl	160[B]	2[B], 12[C]
Methoxychlor	80000[B]	47500[B], 2050[C], 120000[C]
Methyl isothiocyanate	6[B]	-
Methyl parathion	9800[B], 5100[C]	82[B], 2080[C]
Methyl urea	59[C]	-
Metobromuron	60[A],[B], 272[C], 104[E], 100[F]	240[E]

Metoxuron	55[E], 69[F]	44[E]
Metribuzin	95[B], 91[G]	-
Mexacarbate	-	1370[B]
Monolinuron	198[A], 200[B], 284[C], 69[E], 66[F]	40[B], 200[E]
Monuron	163[A], 100[B], 184[C], 50[E], 59[F]	29[B], 133[C], 96[E]
MSMA	-	8.0×10^{-4}[C]
Naphthalene	1300[B], 414[E]	2040[B], 2290[E]
Napropamide	680[B]	-
Neburon	2300[B], 3110[C]	-
Nitralin	960[B]	-
Nitralin ($R_1 = C_3H_7$; $R_2 = CH_3$)	500500[A]	-
Nitrapyrin	420[B], 271[A], 238[A], 172[E]	2590[B], 1050[E]
Nitrofen	-	1240[C]
Norfluorazon	1910[B]	-
Oryzalin [D]	-	-
Oxadiazon	3240[B]	-
Oxamyl	5[E]	0.3[E]
Paraquat	15500[B]	-
Paraquat.2HCl	-	1[C]
Parathion	4800[B], 10650[C]	6400[B], 6450[C],

	1040[E]	8510[E]
p-Chloroaniline	562[C]	-
PCP	-	14300[C]
Pebulate	719[A], 630[B]	-
Pentachlorophenol	900[B]	102000[B]
Permethrin	33300[F]	753[C], 3981000[F]
Phenol	52[E]	29[E]
Phenyl urea	76[C]	-
Phorate	3200[B], 655[E]	823[C], 18200[E]
Phosalone	-	20100[B], 20000[C]
Phosmet	-	677[B], 676[C]
Picloram	13[A], 17[B], 26[C]	2[B], [C]
Profluralin	8600[B]	-
Prometne	74[A], 350[B]	-
Prometryn	311[A], 810[B], 614[C]	-
Pronamide	200[B]	-
Propachlor	265[B], 102[G]	560[B], 41[C]
Propanil	-	106[C]
Propazine	152[A], 160[B], 154[C]	785[B]
Propham	51[A], [B], 88[E]	398[E]
Propoxur	-	33[B], 28[C]
Pyrazon	120[B]	-
Ronnel	-	46400[B], 75900[C]

Silvex (fenoprop)	2600[B]	-
Simazine	159[A], 135[B], 138[C], 47[E]	155[B], 88[C], 32[E]
2,4,5-T	42[A], 40[A], 53[B], 80[C]	4[B], 7[C]
2,4,5-T, butyl ester	-	64000[C]
2,4,5-T, octyl ester	-	909[C]
Tebuthiuron	620[B]	-
Terbacil	51[B], 41[C]	78[C]
Terbufos	-	167[C]
Terbutryn	700[B]	-
Tetrachloroethylene	-	758[B]
Thiabendazole	1720[B]	-
Thimet	3260[C]	-
Toxaphene	-	1700[C]
Triallate	2220[B]	-
Trichlorfon	-	3[B]
1,2,4-Trichlorobenzene	-	15000[B]
Triclopyr	27[B]	3[B]
Triclopyr (butoxyethyl ester)	-	12300[B]
Triclopyr (triethylamine salt)	-	3[B]
Trietazine	600[B]	2200[B]
Trifluralin	13700[B]	220000[B], 1150[C]
Trithion	46600[C]	-

[1]Source of data references:
A: Hamaker and Thompson (1972)
B: Kenaga and Goring (1980)
C: Rao and Davidson (1980)
D: Pionke and DeAngelis (1980)
E: Briggs (1981a)[3]
F: Briggs (1981b)[4]
G: Rao et al. (1983)

[2] Reference D provides K_d values, not K_{oc} or K_{ow}.
[3] Reference E values are given as log K_{am}; we converted them to K_{oc}.
[4] Reference F values are given as K_{am}; we converted them to K_{oc}.

Table 1.--Semi-empirical equations for estimating K_{oc} from solute physical properties

	Calibration[1] Compounds	K_{oc} Range	Number Compounds	r^2	Reference
a. $\log K_{oc} = -0.68 \log S(\mu g/ml) + 4.273$	pn, ha, aa, ch	$10-10^6$	23	0.93	Hassett, 1980
b. $\log K_{oc}$[2] $= -0.557 \log S(\mu mole/L) + 4.277$	ch	$10-10^5$	15	0.99	Chiou, 1979
c. $\log K_{oc} = -0.83 \log S(\text{mole fraction})$[3] $- 0.01(mp-25^oC)$[4] $- 0.93$	pn, ch, ct, cb, op	10^2-10^6	47	0.93	Karickhoff, 1984
d. $\log K_{oc}$[2] $= -0.729 \log S(\text{molar}) - 0.0073\ (mp - 25^oC) + 0.24$	pn, ch	$10-10^5$	12	0.996	Chiou, 1983
e. $\log K_{oc}$[2] $= -0.808 \log [\bar{V}S(\text{molar})]$[5] $- 0.0081\ (mp - 25^oC) - 0.74$	pn, ch	$10-10^5$	12	0.997	Chiou, 1983
f. $\log K_{oc}$[2] $= 0.904 \log K_{ow} - 0.539$	pn, ch	$10-10^5$	12	0.989	Chiou, 1983
g. $\log K_{oc} = 1.029 \log K_{ow} - 0.18$	ch, ct, cb, op, ur, pa	$10-10^5$	13	0.91	Rao, 1982
h. $\log K_{oc} = \log K_{ow} - 0.317$	pn, ha, aa, ch	$10-10^6$	23	0.98	Hassett, 1980
i. $\log K_{oc} = 0.72 \log K_{ow} + 0.49$	ch, mb	10^2-10^4	13	0.95	Schwarzenbach, 1981

[1]pn-polynuclear aromatic hydrocarbons; ha-heteronuclear aromatic hydrocarbons; aa-aromatic amines; ch-chlorinated hydrocarbons; ct-chloro-s-triazines; cb-carbamates; op-organophosphates; ur-uracils; pa-phenoxy acids; mb-methylated benzenes.
[2]Original data expressed as K_{om}; the factor 1.74 was used to convert K_{om} to K_{oc}; $K_{oc} = 1.74\ K_{om}$.
[3]For hydrophobic compounds, S(mole fraction)$\approx$S(molar) x 18/1000.
[4]mp - melting point in degrees celsius; reference temperature 25°C; for liquids mp set at 25°C, crystal term vanishes.
[5]$\bar{V}$ pure solute molar volume (L/mole).

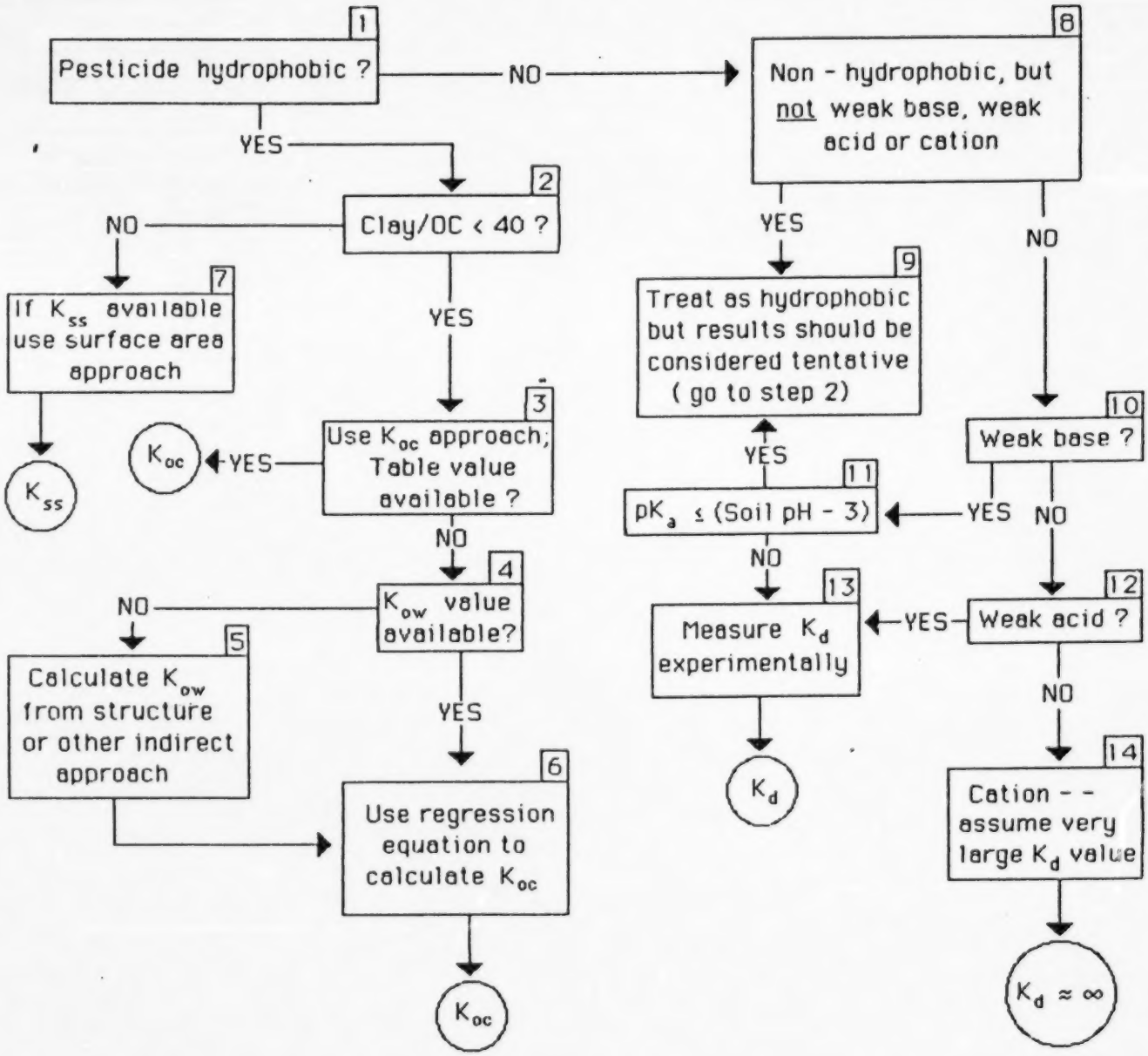

FIG. 1 Decision sequence for obtaining a pesticide coefficient.